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MATRIX ISOLATION OF BORON AND CARBON VAPOR. CONTROL OF CLUSTER FORMATION DURING PREPARATION AND ANNEALING

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Abstract

The formation and recombination of small boron/carbon clusters were studied by *quantitative* Fourier transform infrared (FTIR) spectroscopy. Samples were prepared by evaporation of powder mixtures from a resistively heated oven (3000 K) and isolated at 10 K in solid argon. C_3 and BC_2 disappeared entirely over the course of several annealings. Yields of all the larger clusters (B_JC_{n-J}, $n \geq 4$, $J = 0, 1, 2$) increased during annealing. Clusters with $n \geq 4$ are linear, with the boron atoms of the $J = 1$ and 2 clusters capping the ends of carbon chains; B_2C_{n-2} clusters are inert. During annealing, C_n and BC_{n-1} clusters grow by adding mobile atom, dimer, or trimer to the carbon end of the chain. Dramatic growth of B_2C_2 during the first annealing is consistent with the presence of B atoms and/or BC molecules in the initial matrices. ↳ (do not react to form larger clusters w/ew material)

Introduction

Under the auspices of the U. S. Air Force High Energy Density Matter (HEDM) Program [1], we have pursued the goal of production of a cryogenic matrix with an atom density of $\sim 1 \times 10^{21}$ atoms cm^{-3}, which amounts to ~ 5 mole percent atoms in an inert solid, or an equivalent atom gas pressure of ~ 60 atm at 298 K. This and our companion paper [2] describe qualitative and quantitative analysis of B_JC_{n-J} clusters in prototypical HEDM. Previously, the first conclusive identifications of small boron clusters, BC_2, B_2C, BC_3, and B_2C_2 were reported [3-5]. Observed FTIR fundamentals and isotope shifts were matched with predictions of *ab-initio* theory in those studies.

Verhaegen, Stafford, and Drowart [6] published the first experimental evidence of B_JC_{n-J} 35-years ago. Mass spectrometry was used to measure boron and boron carbide vaporization from graphite Knudsen cells heated by electron bombardment to ~ 2500 K. The vapor pressure of boron at 2200 K was ~ 0.008 torr, 94% atoms, 5% BC_2, 1% B_2C, and 0.07% BC. At the same temperature, boron carbide had about one-half the vapor pressure with 96% atoms, 4% BC_2, 0.1% B_2C. Distributions of anions and cations of B_xC_y with up to 17-atoms have been measured in plumes of laser vaporized boron carbide targets by Becker and Dietze [7]. Their mass spectrometric analysis showed that B_2C^-, B_2C^+, BC_2^-, and BC_2^+ were major components of the plume. Matrix isolated BC_2 has been produced by oven and laser vaporization of carbon/boron mixtures and targets and measured by FTIR [3,8] and ESR [9,10] spectroscopy. Most recently, Wyss, Grutter and Maier [11] isolated BC_2^- and BC^- in neon matrices by sputtering a boron carbide target with Cs^+ and trapping the mass-selected anions in neon matrices. Neutrals were produced by electron photodetachment with uv radiation. Electronic transitions of BC_2 and BC and their anions were studied. The FTIR

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spectrum of the previously identified [3] $\nu_2(a_1)$ fundamental of BC_2 was also observed. The infrared spectrum of BC has never been measured, but a CCSD(T)/cc-pVTZ calculation with quartic force field predicted [12] its vibrational fundamental at 1148 cm^{-1} with intensity of 43 km mol^{-1}. Of the pure boron clusters, only B_3 has been experimentally observed. Li, Van Zee and Weltner [13] identified all four isotopomers of B_3 in argon matrices by FTIR spectroscopy and found that experimental frequencies matched *ab-initio* frequencies of its cyclic geometry. Although *ab-initio* studies of B_n, $n \geq 4$, have been carried out, only geometries and energies have been reported [14,15]. Unlike C_n, B_n for $n \geq 5$ are predicted to have stable 3-dimensional geometries.

Carbon clusters were recently reviewed by Van Orden and Saykally [16]. Cyclic C_6 [17, 18], cyclic C_8 [19, 20], linear C_{11} [21], have recently been identified by their FTIR isotopomer spectroscopy. Most recently, electronic spectra of linear C_{17}, C_{19}, and C_{21} [22] and cyclic C_{10} and cyclic C_{12} [23] isolated in neon matrices were reported, and Raman spectra of linear C_{16}, C_{18}, and C_{20} were reported [24].

Figure 1 shows a Pascal's triangle representation of the boron/carbon system. In the limit of statistical recombination of well mixed atoms, the relative yields of $B_J C_{n-J}$ clusters of given n is given by

$$\rho(B_J C_{n-J})/\rho(C_n) = n!/J!(n-J)![B/C]^J,\qquad(1)$$

where [B/C] is the molar ratio of boron to carbon, and $\rho(i)$ is the column density of species i.

Experimental

Mixtures of boron and carbon powders were evaporated with a resistively heated oven to temperatures $\sim$ 3000 K, and vapors were co-condensed with $\sim$ 1000:1 excess argon at 10 K to form $\sim$ 60 μ thick matrices in about one-hour. Beer's Law enabled quantitative analysis of the various species, $\rho(i) = 2.303\, A_i(experiment)/I_i(theory)$, where $\rho(i)$ is the average column density, which is the average value of the product of the species density and matrix thickness. $A_i(experiment)$ is the integrated intensity of the infrared absorbance of species i, equal to $-log_{10}\, \tau_i(\nu)$, where $\tau_i(\nu)$ is the transmittance at absorption frequency ν. $I_i(theory)$ is the infrared absorption intensity of species i, which by necessity must be obtained by *ab-initio* calculation because experimental values are not available at this time. Fig. 1 indicates values of $I_i(theory)$ calculated by DFT/cc-pVDZ [25-28].

Results and Discussion

Annealing of pure carbon matrices led to disappearance of atoms, dimers and trimers from the initial deposits. The identified products of recombination included cyclic C_6 and cyclic C_8, and linear C_n molecules, $4 \leq n \leq 13$. After annealing to constant composition, the total measurable carbon was found to be as much as twice the initial measurable carbon, indicating that about 50 % of the initially deposited carbon was isolated as atoms and dimers. The cyclic molecules, the dominant condensation products, amounted to as much as $\sim$ 60% of total carbon in the fully annealed matrices.

In matrices containing boron, linear C_3 and cyclic BC_2, B_2C, and B_3, constituted about 80% of the total observable boron and carbon in the initially deposited matrix. The observation of approximately statistical distributions [Equation (1)] in clusters with n = 3, 4, and 5 in the initially deposited matrices implies that these smaller clusters form by random condensation of well-mixed atoms, uninfluenced by their relative energies, the energies of their precursors, or preferential kinetics pathways that could otherwise distort the statistics.
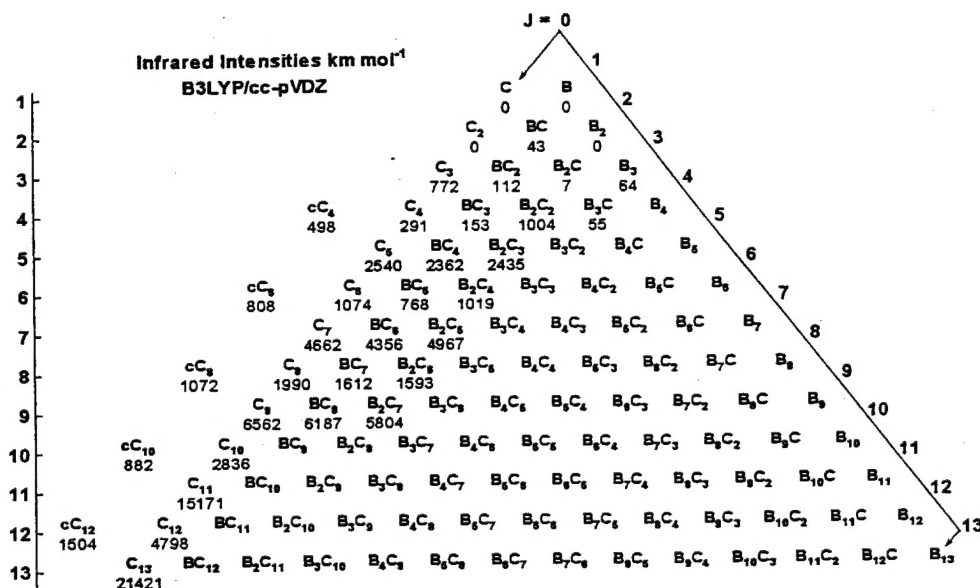
J = 0
1
2
3
4
5
6
7
8
9
10
11
12
13

C 0   B 0

C$_2$ 0   BC 43   B$_2$ 0

C$_3$ 772   BC$_2$ 112   B$_2$C 7   B$_3$ 64

cC$_4$ 498   C$_4$ 291   BC$_3$ 153   B$_2$C$_2$ 1004   B$_3$C 55   B$_4$

C$_5$ 2540   BC$_4$ 2362   B$_2$C$_3$ 2435   B$_3$C$_2$ B$_4$C   B$_5$

cC$_6$ 808   C$_6$ 1074   BC$_5$ 768   B$_2$C$_4$ 1019   B$_3$C$_3$ B$_4$C$_2$ B$_5$C   B$_6$

C$_7$ 4662   BC$_6$ 4356   B$_2$C$_5$ 4967   B$_3$C$_4$ B$_4$C$_3$ B$_5$C$_2$ B$_6$C   B$_7$

cC$_8$ 1072   C$_8$ 1990   BC$_7$ 1612   B$_2$C$_6$ 1593   B$_3$C$_5$ B$_4$C$_4$ B$_5$C$_3$ B$_6$C$_2$ B$_7$C   B$_8$

C$_9$ 6562   BC$_8$ 6187   B$_2$C$_7$ 5804   B$_3$C$_6$ B$_4$C$_5$ B$_5$C$_4$ B$_6$C$_3$ B$_7$C$_2$ B$_8$C   B$_9$

cC$_{10}$ 882   C$_{10}$ 2836   BC$_9$ B$_2$C$_8$ B$_3$C$_7$ B$_4$C$_6$ B$_5$C$_5$ B$_6$C$_4$ B$_7$C$_3$ B$_8$C$_2$ B$_9$C   B$_{10}$

C$_{11}$ 15171   BC$_{10}$ B$_2$C$_9$ B$_3$C$_8$ B$_4$C$_7$ B$_5$C$_6$ B$_6$C$_5$ B$_7$C$_4$ B$_8$C$_3$ B$_9$C$_2$ B$_{10}$C   B$_{11}$

cC$_{12}$ 1504   C$_{12}$ 4798   BC$_{11}$ B$_2$C$_{10}$ B$_3$C$_9$ B$_4$C$_8$ B$_5$C$_7$ B$_6$C$_6$ B$_7$C$_5$ B$_8$C$_4$ B$_9$C$_3$ B$_{10}$C$_2$ B$_{11}$C   B$_{12}$

C$_{13}$ 21421   BC$_{12}$ B$_2$C$_{11}$ B$_3$C$_{10}$ B$_4$C$_9$ B$_6$C$_9$ B$_6$C$_7$ B$_7$C$_6$ B$_8$C$_5$ B$_9$C$_4$ B$_{10}$C$_3$ B$_{11}$C$_2$ B$_{12}$C   B$_{13}$

Figure 1. Representation of the B_JC_{n-J} (n = 1 - 13, J = 0 - n) system by Pascal's triangle. Numbers below molecular formulas denote the _ab-initio_ intensities of the most intense infrared stretching fundamentals, Refs. [25] – [28]. Cyclic carbon clusters are removed from the triangle to the left.
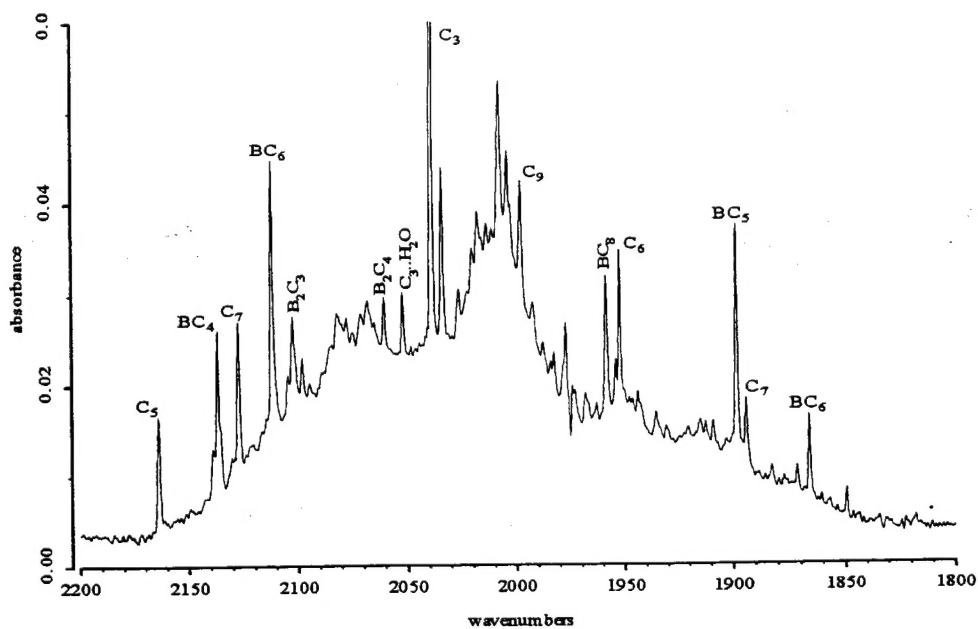
Figure 2. Survey spectrum of matrix containing carbon and boron at natural abundance with [B/C] ~ 1/3 after three annealings. All of the peaks indicated grow upon annealing except C_3. Fundamentals of BC_{n-1} for n = 5, 6, 7, and 9 are similarly red-shifted from fundamentals of linear C_n and their experimental absorbances are all slightly greater in this matrix. Two fundamentals of BC_6 are observed at 2112 and 1866 cm^{-1}, red-shifted from the two fundamentals of linear C_7.

B_2C_{n-2} clusters, once formed, were inert to further condensation upon annealing. Thus, energy loss by recombination during preparation of high energy density matrices (HEDM) is minimized in matrices with large B/C ratios. For example, when B/C ~2, any recombination that does occur during co-deposition would tend to produce B_2C, a high-energy molecule that is inert in the cryogenic environment. In pure boron HEDM, the cyclic B_3 molecule may be similarly inert, which would suggest that energy loss by recombination will also stop at a B_3 "island of stability." Continuing experimental work to produce five-mole percent pure boron HEDM is concentrating on development of a resistively heated high-flux boron atom source, the "boron cannon", and production of higher density matrices.

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MATRIX ISOLATION OF BORON AND CARBON VAPOR.

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Abstract

This report supplements the companion paper published in this volume [1]. Details about the FTIR quantitative analysis of the disappearance and formation of clusters during annealing of solid argon matrices containing boron and carbon species are presented.

Introduction

The companion paper [1] summarized the literature of small boron clusters, about $B_J C_{n-J}$ (n = 2 to 10, J = 0, 1, 2, 3) and described the formation of clusters during preparation and annealing of solid argon. This report presents additional details.

Experimental

A precision matched pair of matrices was prepared as described in Ref. [1] with two different boron isotopic compositions and natural abundance carbon. Matrix (a) contained natural abundance boron, $^{11}B/^{10}B = 4.0$, and matrix (b) contained boron with an inverted isotope ratio, $^{11}B/^{10}B = 0.37$. Each matrix had a [C/B] molar ratio of ~ 3.0, a thickness of ~ 60 m, and very similar absolute amounts of each element. Each matrix was annealed repeatedly according to the same annealing protocol given in the caption of Figure 1.

Results and Discussion

Figure 1 shows the annealing behaviors of the FTIR bands belonging to BC_2, BC_3 and B_2C_2 for each of the matrices. Cyclic BC_3 disappears entirely when one of its carbon atoms is attacked by a radical species. One of the B-C bonds is broken, and the BC_3 ring ⟶ with opens. The dramatic appearance of B_2C_2 during the first annealing is consistent a mechanism involving recombination of BC, whose density lies below the limit of detection, or condensation of B atoms with BC_2.

Figure 2 shows the annealing behaviors of the $^{11}B_J{}^{12}C^{n-1}$ clusters, n = 3 to 9 and J = 0, 1, 2 that were measured in matrix (a). Loss of clusters during the sixth annealing by matrix sublimation is generally greatest for C_n and smallest for B_2C_{n-2}, which is consistent with a stratified matrix with a higher [C/B] ratio near the subliming surface. Apparently, boron evaporates more rapidly than carbon during the early stages of oven evaporation, resulting in boron-rich layers near the substrate.

Column densities of the trimer clusters in the initially deposited matrices are in the ratio $\rho(C_3):\rho(BC_2):\rho(B_2C):\rho(B_3) \approx 1.0:1.5:0.5: < 0.05$, where only the upper limit for $\rho(B_3)$ may be determined because it was not observed. This is consistent with formation of the trimers by statistical condensation from a matrix with [B/C] ~ 1/3, which would produce a 1.0:1.0:0.33:0.05 distribution, $\rho(B_J C_{n-J})/\rho(C_n) = n!/J!(n-J)![B/C]^J$, Eq. (1), Ref. [1].

Agreement between distributions implies trimers form by random condensation of well-mixed atoms, uninfluenced by the relative energies of the trimers, the energies of their precursors, or preferential kinetics pathways that could otherwise distort the statistics. Linear C_3 and cyclic BC_2, disappeared entirely when the matrices were repeatedly annealed to
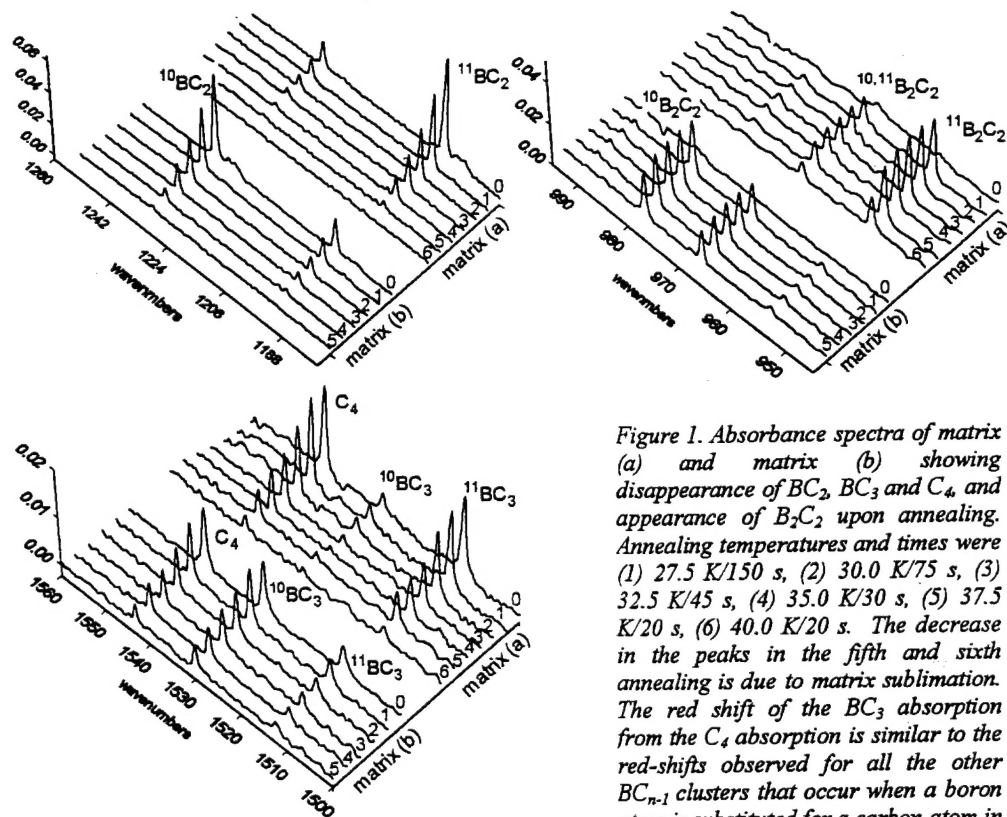
Figure labels (top left spectrum): $^{10}BC_2$, $^{11}BC_2$, wavenumbers 1260, 1242, 1224, 1206, 1188, matrix (a), matrix (b), 0.06, 0.04, 0.02, 0.00, annealing steps 6 5 4 3 2 1 0

(top right spectrum): $^{10}B_2C_2$, $^{10,11}B_2C_2$, $^{11}B_2C_2$, wavenumbers 990, 980, 970, 960, 950, matrix (a), matrix (b), 0.04, 0.02, 0.00, annealing steps 6 5 4 3 2 1 0

(bottom left spectrum): C_4, $^{10}BC_3$, $^{11}BC_3$, wavenumbers 1550, 1540, 1530, 1520, 1510, 1500, matrix (a), matrix (b), 0.02, 0.01, 0.00

Figure 1. Absorbance spectra of matrix (a) and matrix (b) showing disappearance of BC_2, BC_3 and C_4, and appearance of B_2C_2 upon annealing. Annealing temperatures and times were (1) 27.5 K/150 s, (2) 30.0 K/75 s, (3) 32.5 K/45 s, (4) 35.0 K/30 s, (5) 37.5 K/20 s, (6) 40.0 K/20 s. The decrease in the peaks in the fifth and sixth annealing is due to matrix sublimation. The red shift of the BC_3 absorption from the C_4 absorption is similar to the red-shifts observed for all the other BC_{n-1} clusters that occur when a boron atom is substituted for a carbon atom in a C_n cluster.

temperatures between 25 K and 35 K, but cyclic B_2C was inert. Linear C_4 and BC_3 (BCCC) disappeared more slowly, and linear B_2C_2 (BCCB) grew to ~ 95% of its final value during the first annealing. Once formed, B_2C_2, like B_2C, was also inert to further reaction.

Figure 3 shows the absolute column densities of the analyzed clusters that (was) obtained by transformation of the Fig. 2 data with Beer's law and theoretical intensities shown in Fig. 1, Ref [1]. The BC molecule was not observed, but its upper limit column density was established to be somewhat larger than that of B_2C_2.

The sources of B_2C_2 are from condensation of atom plus trimer (B + BC_2 but not C + B_2C) or dimer + dimer (BC + BC but not B_2 + C_2). Although BC was not observed, the upper limit of ρ(BC) is larger than ρ(B_2C_2) so that BC cannot be ruled out as a source of B_2C_2. The growth of B_2C_2 is consistent with of the presence of BC and/or B in the originally deposited matrix in an amount at least as great as the growth of B_2C_2.

Figures 1 and 2 show that C_4 and BC_3 do not change during the first annealing but begin to disappear in subsequent annealings. This indicates that a source for these tetramers, atom + trimer and/or dimer + dimer, operates during the first annealing .

Figure 2 shows that linear C_5, BC_4 (BCCCC) and B_2C_3 (BCCCB) and larger linear clusters all grew upon annealing. The sources of B_2C_3 are dimer + trimer (BC + BC_2 but not B_2 + C_3) and atom + tetramer (B + BC_3 but not C + B_2C_2). Since ρ(BC_2) ~ 5ρ(BC_3) in the initially deposited matrix, the BC + BC_2 source is dominant. Growth of B_2C_3 is consistent with the presence of BC in the initially deposited matrix in an amount at least as great as the amount by which B_2C_3 grows.
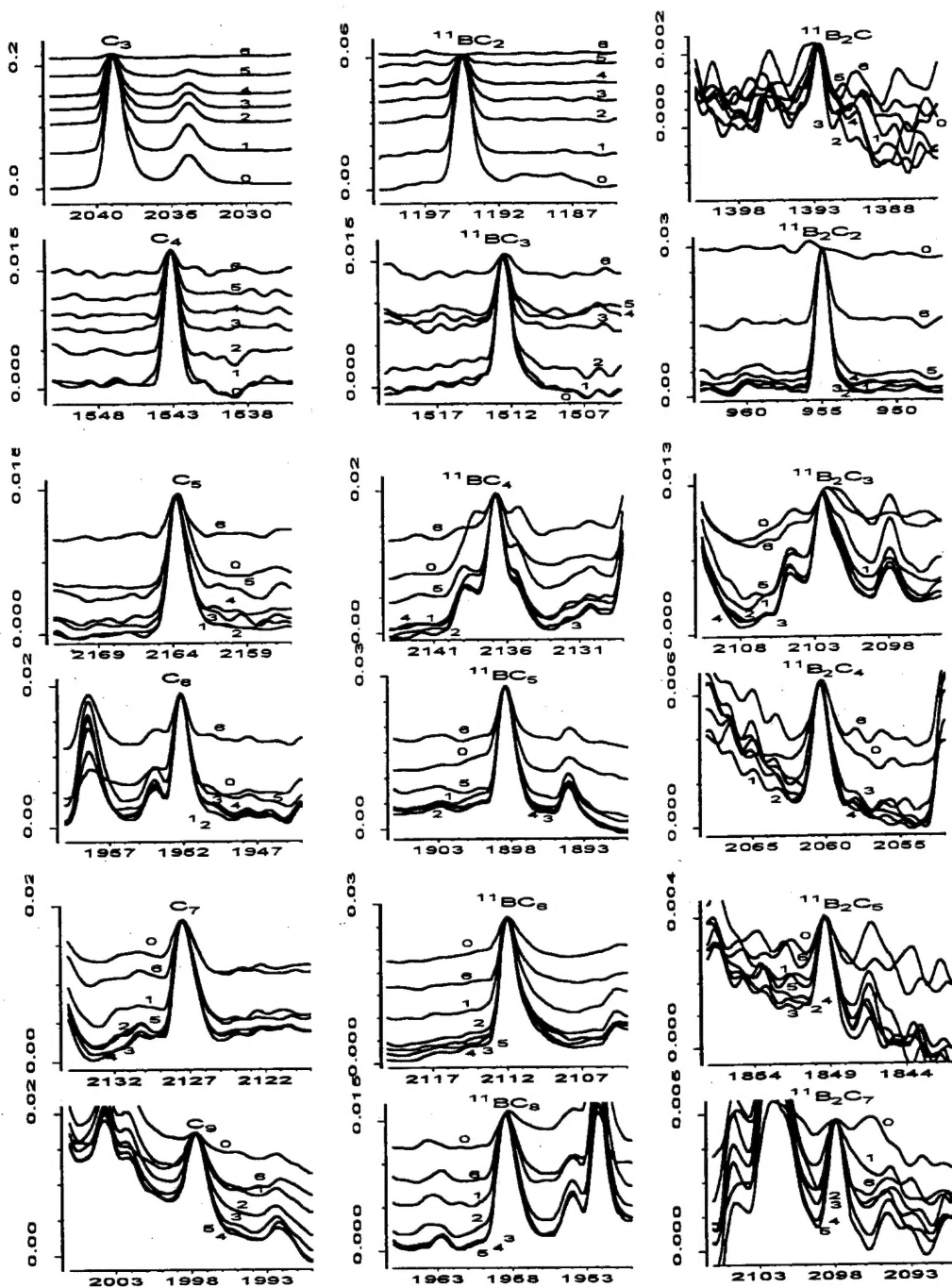
Figure 1. Annealing behaviors of $^{11}B_J{}^{12}C_{n-J}$ species in matrix (a), which contained natural abundance carbon and boron, $^{11}B/^{10}B=80/20$, $^{12}C/^{13}C=99/1$, with $[C/B] \sim 3$. Spectra labeled '0' were obtained from the originally deposited matrix, and spectra labeled '1' to '6' were obtained after successive annealings. During the 6th annealing (at 40 K for 20 seconds), almost half the matrix evaporates.
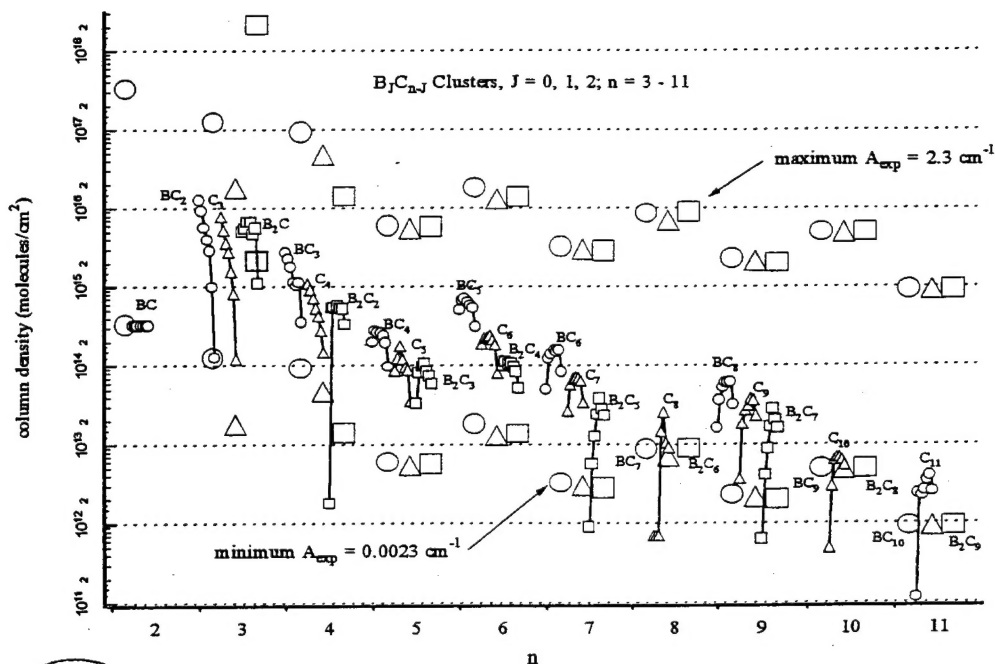
Figure 2. *Distributions of B_JC_{n-J} clusters, J = 0, 1, 2; n = 3 - 11. Circles, triangles and squares represent BC_{n-1}, C_n, and BC_{n-2} clusters, respectively. Large symbols denote upper and lower limits of measurement, based on a nominal minimum measurable absorbance of 0.0023 cm^{-1}, and a maximum absorbance for linearity of Beer's law of 2.3 cm^{-1} (1% transmittance). Small symbols denote measured quantities in the initial matrix, and in six annealed matrices. Some of the larger clusters (n = 8, 10, 11) have not been identified, BC_7, B_2C_6, BC_9, B_2C_8, BC_{10}, B_2C_9.*

Growth of BC_4 occurs primarily by $BC + C_3$ rather than $B + C_4$ or $C + BC_3$ because $\rho(C_3) \sim 10\rho(C_4)$ and $\rho(C_3) \sim 2\rho(BC_3)$. Growth of C_5 occurs by $C + C_4$ and $C_2 + C_3$, which establishes the presence of C and/or C_2 in the original matrix in an amount at least as great as C_5 growth.

Conclusions

Disappearance of triangular BC_2 requires breaking of one of its B-C bonds when one of its carbon atoms is attacked. The major reorganization of electronic energy involved in opening the ring appears to occur with little (< ~3 kcal mol^{-1}) or no energy barrier, which makes this small molecule a candidate for an interesting *ab-initio* study of unusual reactivity at low temperature. Annealing kinetics of disappearance of C_3 and BC_2, and of appearance of B_2C, C_4, BC_3, $B2C_2$, C_5, BC_4, and B_2C_3 unequivocally establishes the presence of atoms and dimers in the originally deposited matrix. About 80% or more of the initially deposited HEDM existed as atoms, dimers and trimers. Molecules with two boron atoms are immune from radical attack and condensation during annealing.

Reference

1. C. W. Larson, J. Harper, J. D. Presilla-Márquez, Poster Paper, This Volume.